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FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,  
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GR, HU, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI  
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(54) Title: IMPROVEMENTS IN METHODS OF MANUFACTURING SUBSTRATES

(57) Abstract: The present invention relates to improvements in methods of manufacture of substrates which can be used in varying shapes and sizes for various authenticating or security applications, which combine the advantages of indicia formed from metallisation or demetallisation of a security element and the colourshift effects of liquid crystal materials. The invention therefore provides a method of manufacturing a substrate comprising the steps of applying a darkly coloured resist to at least a part of a metallic layer on one side of a substantially transparent polymeric film, removing metal from areas not covered by the resist to form demetallised regions and applying a polymeric liquid crystal material over the resist and the demetallised regions.

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IMPROVEMENTS IN METHODS OF MANUFACTURING SUBSTRATES

The present invention relates to improvements  
in methods of manufacture of substrates which can be  
5 used in varying shapes and sizes for various  
authenticating or security applications, which  
combine the advantages of indicia formed from  
metallisation or demetallisation of a security  
element and the colourshift effects of liquid  
10 crystal materials.

The increasing popularity of colour  
photocopiers and other imaging systems and the  
improving technical quality of colour photocopies  
15 has led to an increase in the counterfeiting of bank  
notes, passports and identification cards etc. There  
is, therefore, a need to add additional  
authenticating or security features to existing  
features. Steps have already been taken to introduce  
20 optically variable features into such documentation  
which cannot be reproduced by a photocopier. There  
is also a demand to introduce features which are  
discernible by the naked eye but which are  
"invisible" to, or viewed differently, by a  
25 photocopier. Since a photocopying process typically  
involves scattering high energy light off an  
original document containing the image to be copied,  
one solution would be to incorporate one or more  
features into the document which have a different  
30 perception in reflected and transmitted light, an  
example being watermarks and enhancements thereof.

It is known that certain liquid crystal  
materials exhibit a difference in colour when viewed  
35 in transmission and reflection as well as an

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angularly dependent coloured reflection. Liquid crystal materials have been incorporated into documents, identification cards and other security elements with a view to creating distinctive optical characteristics. EP-A-0435029 is concerned with a data carrier, such as an identification card, which comprises a liquid crystal polymer layer or film in the data carrier. The liquid crystal polymer is in solid form at room temperature and is typically within a laminate structure. The intention is that the liquid crystal layer, which is applied to a black background, will demonstrate a high degree of colour purity in the reflected spectrum for all viewing angles. Automatic testing for verification of authenticity is described using the wavelength and polarisation properties of the reflected light in a single combined measurement. This has the disadvantage of being optically complex using a single absolute reflective measurement requiring a uniform liquid crystal area on a black background. AU-488,652 is also concerned with preventing counterfeit copies by introducing a distinctive optically-variable feature into a security element. This patent discloses the use of a liquid crystal "ink" laminated between two layers of plastic sheet. The liquid crystal is coated on a black background so that only the reflected wavelengths of light are seen as a colour. The patent is primarily crystals which have the characteristic of changing colour with variation in temperature.

Cholesteric liquid crystals have certain unique properties in the chiral nematic phase. It is the chiral nematic phase which produces an angularly dependent coloured reflection and a difference in

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colour when viewed in either transmission or reflection. Cholesteric liquid crystals form a helical structure which reflects circularly polarised light over a narrow band of wavelengths.

5      The wavelength is a function of the pitch of the helical structure which is formed by alignment within the liquid crystal material. An example of such a structure is depicted in Figure 1 with the cholesteric helical axis in the direction of the arrow X. The reflection wavelength can be tuned by appropriate choice of chemical composition of the liquid crystal. The materials can be chosen to be temperature sensitive or insensitive. Both handednesses of circularly polarised light can be

10     reflected by choice of the correct materials and thus high reflectivities at specific wavelengths can be achieved with double layers of liquid crystals. The wavelength of reflected light is also dependent on the angle of incidence, which results in a colour change perceived by the viewer as the device is

15     tilted (Figure 2).

On a dark background, only the reflective effect is observed, since little light is being transmitted from behind. When the dark background is removed or not present and the device is viewed in transmission, the intensity of the transmitted colour swamps the reflective colour.

30       Of the light which is not reflected, a small proportion is absorbed and the remainder is transmitted through the liquid crystal material 3. When correctly configured there is a dramatic change between the transmitted colour in the direction of arrow Y and reflected colour in the direction of

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arrow Z (Figure 3). The region on either side of the liquid crystal layer 3 in Figure 3 is a transparent polymer or glass. To achieve this effect the area of the substrate which is occupied by the liquid  
5 crystal must be transparent or translucent. The transmitted and reflected colours are complementary, for example, a green reflected colour produces a magenta transmitted colour.

10

In the field of banknotes, and security elements or threads in particular, the use of demetallised indicia such as described in EP-A-319157 has proved to be highly effective in reducing  
15 counterfeiting. However, in the security business it is always advantageous to continually strive to find new and further improved anti-counterfeit security features. It is desired to use the highly advantageous characteristics of demetallised  
20 characters and colour shift effects from liquid crystal materials.

According to the invention there is provided a method of manufacturing a substrate comprising the  
25 steps of applying a darkly coloured resist to at least a part of a metallic layer on one side of a substantially transparent polymeric film, removing metal from areas not covered by the resist to form demetallised regions and applying a polymeric liquid  
30 crystal material over the resist and the demetallised regions.

The invention also provides a substrate made by this method.

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A preferred embodiment of the present invention will now be described, by way of example only, with reference to the accompanying drawings in which:-

5       Figure 1 depicts chiral nematic alignment of a cholesteric liquid crystal material;

10      Figure 2 shows how the reflection from a cholesteric liquid crystal material varies with the angle of incidence;

15      Figure 3 depicts the transmission and reflection of light incident on a liquid crystal material;

20      Figures 4 and 5 are cross sections across the width of two alternate elongate authenticating device formed by the present invention; and

25      Figure 6 is a plan view of the elongate authenticating device of Figure 5.

25      Figure 7 is a cross section of a further embodiment of substrate 10 forming part of a laminated structure;

30      Figure 8 is a cross section of a yet further embodiment of substrate 10.

35      Figures 1 to 3 have already been described in detail as background to the present invention.

.. Referring now to Figure 4, there is illustrated a substrate 10 formed by the method of the present invention for use in security or authenticating

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devices. The method requires a metallised film comprising a substantially clear polymeric film 11 of PET or the like, which has an opaque layer of metal 12 on a first side thereof. A suitable 5 pre-metallised film is metallised MELINEX S film from DuPont of preferably 19 $\mu$ m thickness.

The metal layer 12 is printed with a resist 13 which contains a black or dark dye or pigment. 10 Suitable resists include the dye BASF Neozapon X51 or the pigment (well dispersed) "Carbon Black 7" mixed into a material with both good adhesion to metal and caustic resistance. The dye loading can be up to 50% (by weight) of the final coat of resist 15 13 depending on coat thickness and desired blackness. An example of a class of suitable resist materials is vinyl chlorides/vinyl acetate copolymers such as Union Carbide Ucar resins, Sun VHL 31534, or Wacker Vinnol E 15/45m. The printed 20 metallised film 11 is then partially demetallised, according to a known demetallisation process using a caustic wash which removes the metal in the regions not printed with the resist 13. The remaining 25 regions coated with resist 13 provide a black layer which is visible when the demetallised film 11 is viewed from its first side (along arrow Y) interspersed with clear regions. The shiny metal of 30 the remaining parts of the metallic layer 12 are only visible from an opposite side of the demetallised film 11 (along arrow X). The resist 13 may be printed in the form of the indicia 15 (see Figure 6) such as words, numerals, patterns and the like; in which case the resulting indicia 14 will be positively metallised, with the metal still covered 35 by the dark or black resist 13. Alternatively the

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resist 13 may be printed so as to form indicia negatively, in which case the resulting indicia 14 will be provided by the demetallised regions. The indicia 14, however formed, are clearly visible from 5 both sides, especially in transmitted light, due to the contrast between the regions of the metal which have been removed and the remaining opaque regions.

A layer 15 of polymeric liquid crystal material 10 is then coated, transferred or laminated to the demetallised film 11 over the remaining parts of the black resist layer 13 and the demetallised regions. This has the effect of producing a highly visible colour shift effect when the finished substrate 10 15 is viewed in reflection from the first side (along arrow Y); and a metallic shiny partial coating when viewed from the other side (along arrow X). Additionally clear positive or negative indicia 14 can be seen in transmission from either side. A 20 layer of a suitable adhesive 16 may be required, for this process, applied between the black resist layer 13 and the liquid crystal layer 15.

When the aforementioned substrate 10, or a 25 strip or thread made therefrom, is included in paper, the remaining metal of layer 12 is not directly visible. It is hidden either by the masking coat of resist 13 or the paper, to which it provides opacity, thereby enabling the contrast 30 between the demetallised and metallised areas to be clearly seen.

If a metallic effect is not desired, when 35 viewed from the back of the paper, an additional masking coat may be used as well as the black layer

of resist 13 and a suitable material for such a masking coat would be Coates 3188XSN or Coates Heliovyl White S90 353. A typical coat weight is suggested to be in the region of 2GSM.

5

Whilst the use of a black, or very dark dye, may give rise to the most strong colour shift effects, other effects may be generated by the use of a dyed resist of other colours or a combination 10 of colours giving rise to differing apparent colour shift colours.

Optionally, a further protective layer 17 may be laminated to or coated over the liquid crystal 15 layer 15. Such a layer 17 may be a PET laminate or an anti-scratch coating. A suitable anti-scratch coating would be Wacker Vinnol E 15/45M.

The black dye or pigment in the resist 13 may 20 be a conducting material, such as carbon black, to produce a machine-readable or conducting layer. Alternatively it may be a magnetic material, such as magnetite, to produce a machine readable magnetic 25 layer. The layers may be continuous or discontinuous and may be of the forms described in EP-A-0516790 or WO-A-9825236 for example.

In a further embodiment of the invention shown 30 in Figure 5, only some parts of the layer of resist 13 contain a dark dye or pigment and some parts 18 are substantially clear containing low concentrations of, or no, dye/pigment. When viewed from the first side (along arrow Y), the metal of the metallic layer 12 can clearly be seen in the 35 regions of remaining clear resist 18, unaffected by

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the liquid crystal layer 17. The colourshift effect can only be seen in the darkly coloured resist regions 13. This is shown in Figure 6.

5       The clear resist regions 18 may also contain a fluorescent, luminescent or phosphorescent material so that, whilst the metallic layer 12 can be seen as metallic in normal lighting in those regions, under UV lighting the regions 18 have a definite colour.

10      Fluorescent materials may be used in separate layers of coatings of the resist. For example, a fluorescent material may be provided in the form of a separate layer of coating over the top of the 15 resist regions 13, 17. Alternatively a fluorescent material may be provided as a separate layer of coating on the back (second side) of the substrate 10 (over the surface of film 11 opposite to the metallised surface). Where a fluorescent material is 20 present in the clear resist regions 18 and a coating is applied to the front or back of the substrate 10 the colour at which that fluorescent material fluoresces may be the same or different to that at which the material used in the coating fluoresces, 25 to obtain different visual effects. A fluorescent material may also be present in the dark resist regions 13, the colour at which that material fluoresces being the same or different to that at which a fluorescent material in the clear resist 30 regions 17 and/or in the coatings on the front or back fluoresce.

35      Additionally, in the regions 18 where the metal is visible under the clear resist 18 a holographic structure can be incorporated into the metallic

- 10 -

layer.

Another effect provided by the invention is that, when viewed off-axis, the colour of the liquid crystal changes slightly as the substrate 10 is rotated. When the substrate is overcoated with an adhesive or anti-scratch coating the colour change is reduced. A water based adhesive, such as a vinyl acetate emulsion, would be suitable. Thus, if the adhesive/anti-scratch coating is applied in the form of a pattern or design, then the coated/uncoated regions can appear as different colours off-axis. When the uncoated regions change colour on movement of the element 10 the contrast is seen more clearly.

15

Another effect which can be usefully used is that, when the substrate 10 is stretched, it changes colour (irreversibly). The colour goes to longer wavelengths (eg green goes to red) and retains its colour shifting capability (eg red now goes to green off-axis).

25 The use of fluorescent, luminescent or phosphorescent materials in the clear parts 18 of the layer of resist 13 enable interesting effects to be produced.

30 The substrate 10 produced by this method can be slit or cut into patches, foils, stripes, strips or threads for incorporation into plastic or paper substrates in accordance with known methods. Whilst these are preferably partially embedded into a paper or plastic substrate, they may be applied to a substrate or wholly embedded within.

35

It will be further understood by those skilled in the art that the proposed method could be used in combination with existing approaches for the manufacture of thread. Examples of suitable 5 constructions that can be used include, but are not limited to, those cited within EP-A-516790, WO-A-9825236, and WO-A-9928852. Figure 7 illustrates how substrate 10 can be enhanced by laminating the basic structure described above to a further structure and 10 Figure 8 shows a more integrated approach.

Figure 7 shows a second machine-readable construction laminated to the basic structure. The machine-readable construction comprises a polymeric 15 film 11, such as a metallised 12 $\mu$ m PET base 11, which has been selectively demetallised. In this example two "tramlines" 30 of metal 12 have been left along each edge of the construction but other variants are possible as illustrated within the 20 cited prior art. The "tramlines" 30 are such that when the final construction is laminated to substrate 10 they are coincident with only metallised regions. A protective layer 20 may be applied onto the "tramlines" 30 to prevent the metal 25 being corroded by the magnetic layer 21, which is applied next. The magnetic material is only applied over the tramlines 30 so as not to obscure the indicia formed with the substrate 10. A suitable protective layer 20 is VHL31534 supplied by Sun 30 Chemical applied with coat weight of 2gsm. A suitable magnetic material 21 is FX 1021 supplied by Ferron applied with a coat weight of 2-6 gsm. On to this a suitable laminating adhesive 19 is applied, 35 this may be the same as for layer 16 in the previous constructions. The whole construction is then

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laminated to the basic structure comprising layers 11, 12, 13, 16, 15 to form the final substrate 10. If a high durability substrate 10 is required it may be preferable to apply a further laminate layer onto 5 the polymer liquid crystal layer as described in previous examples.

Figure 8 shows another alternative approach to forming a machine-readable construction of substrate 10. Here a 12 µm metallised PET base layer 11 is demetallised with a suitable design 12 again ensuring tramlines 30 are left along each edge of the thread. As described above a black resist 13 is used during the demetallisation process. On to a 15 coloured, preferably black, resist 13 a protective layer 20 may be applied prior to application of a magnetic layer 21. The protective layer 20 may optionally be pigmented. Suitable materials and coat weights are as described for Figure 7. Finally 20 a layer of polymer liquid crystal 15 is laminated on to the top using a laminating adhesive 16 as previously described.

In both the examples above the magnetic material 21 is applied as tramlines along both edges of the thread. It should also be noted that the magnetic material 21 could be applied to any of the examples described herein in any manner so long as it does not obscure the demetallised regions and 30 consequently obscure the indicia 14. Preferably the magnetic material is applied over the resist 13,17 or on the back of the film 11. Various alternative constructions can be used.

35 The substrate 10, or security thread made

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therefrom, described in any of the above embodiments may be used in security paper such as bank notes.

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CLAIMS:

1. A method of manufacturing a substrate (10) comprising the steps of applying a darkly coloured resist (13) to at least a part of a metallic layer (12) on a first side of a substantially transparent polymeric film (11), removing metal from areas not covered by the resist (13) to form demetallised regions and applying a polymeric liquid crystal material (15) over the resist (13) and the demetallised regions.  
5
2. A method as claimed in claim 1 in which the resist (13) contains a dye or pigment which is black or dark.  
15
3. A method as claimed in claim 1 or claim 2, further comprising the step of applying a substantially clear resist (15) to at least another part of the metallic layer (12).  
20
4. A method as claimed in any one of the preceding claims in which the removal of metal in the demetallisation process is carried out with a caustic wash.  
25
5. A method as claimed in any one of the preceding claims in which negative indicia (14) are formed by the demetallised regions.  
30
6. A method as claimed in any one of claims 1 to 4 in which positive indicia (14) are formed by the resist covered regions.
- 35 7. A method as claimed in any one of the preceding

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claims in which the polymeric liquid crystal layer (15) is applied by a coating process.

8. A method as claimed in any one of claims 1 to 6  
5 in which the polymeric liquid crystal layer (15) is applied by a transfer process.

9. A method as claimed in any one of claims 1 to 6  
10 in which the polymeric liquid crystal layer (15) is applied by a lamination process.

10. A method as claimed in any one of the preceding claims in which the resist (13) incorporates a conducting material to produce a machine-readable  
15 conducting layer.

11. A method as claimed in any one of the preceding claims in which the resist (13) incorporates magnetic material to produce a machine readable  
20 magnetic layer.

12. A method as claimed in any one of claims 1 to 10 in which magnetic material is located in a continuous or discontinuous layer over the resist  
25 (13).

13. A method as claimed in any one of claims 1 to 10 in which magnetic material is located in a continuous or discontinuous layer on a second side  
30 of the polymeric film (11).

14. A method as claimed in any one of the preceding claims in which the resist (13) comprises a plurality of different colours.

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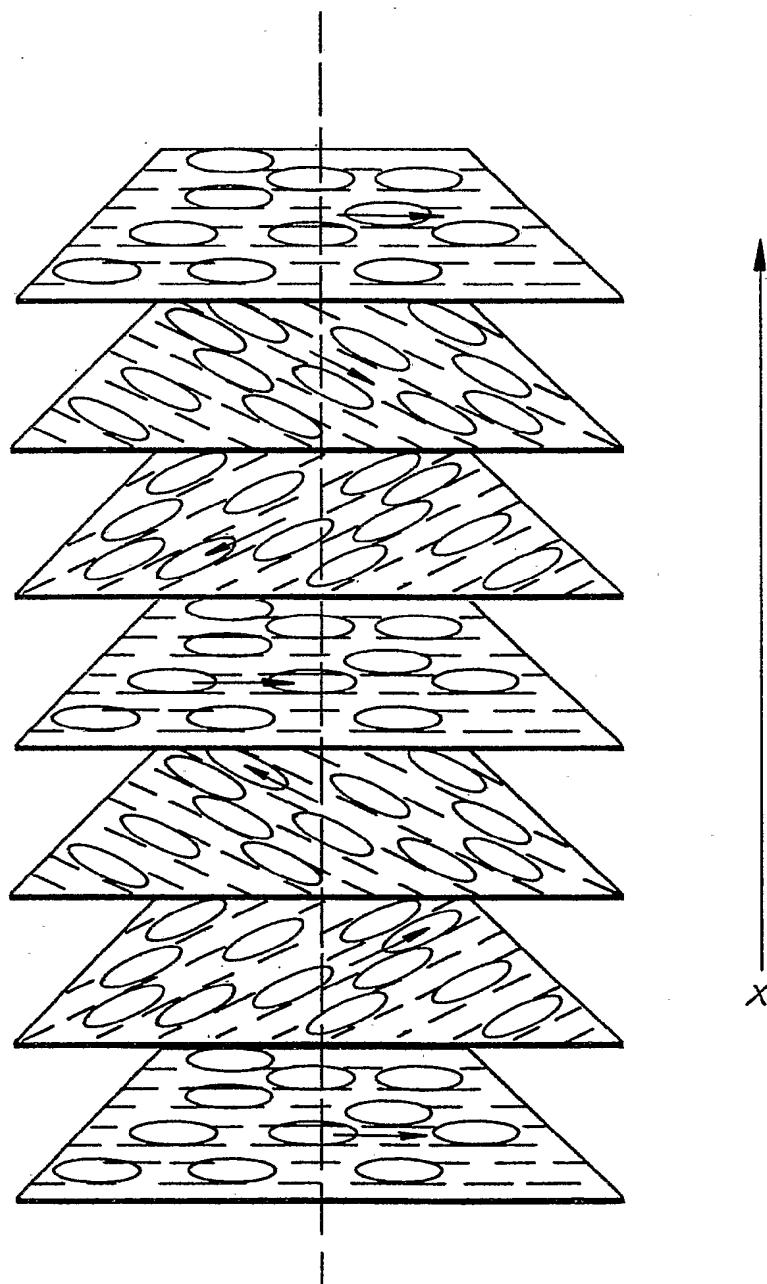
15. A method as claimed in any one of the preceding claims in which a holographic structure is incorporated.
- 5 16. A method as claimed in any one of the preceding claims in which fluorescent, luminescent and/or phosphorescent material is incorporated in the resist (13).
- 10 17. A method as claimed in an one of the preceding claims in which a fluorescent, luminescent and/or phosphorescent material is incorporated in the clear resist (18).
- 15 18. A method as claimed in an one of the preceding claims in which a fluorescent material is incorporated in a layer over the resist (13,18).
- 20 19. A method as claimed in an one of the preceding claims in which a fluorescent material is incorporated in a layer on a second side of the film (11).
- 25 20. A method as claimed in any one of the preceding claims further accompanying the step of laminating to a second side of the film (11) a machine readable construction having a partially metallised or demetallised polymeric film (11) having a continuous strip (30) of metal (12) along each edge coincident with resist covered metal regions, in which a magnetic material is present in the continuous strips.
- 30 35 21. A substrate (10) formed by the method of any one of the preceding claims.

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22. A patch, foil, stripe, strip or thread formed from the substrate (10) of claim 21.
23. Security paper incorporating one or more of the path, foil, stripe, strip or thread of claim 22.  
5
24. A bank note made from the security paper of claim 23.

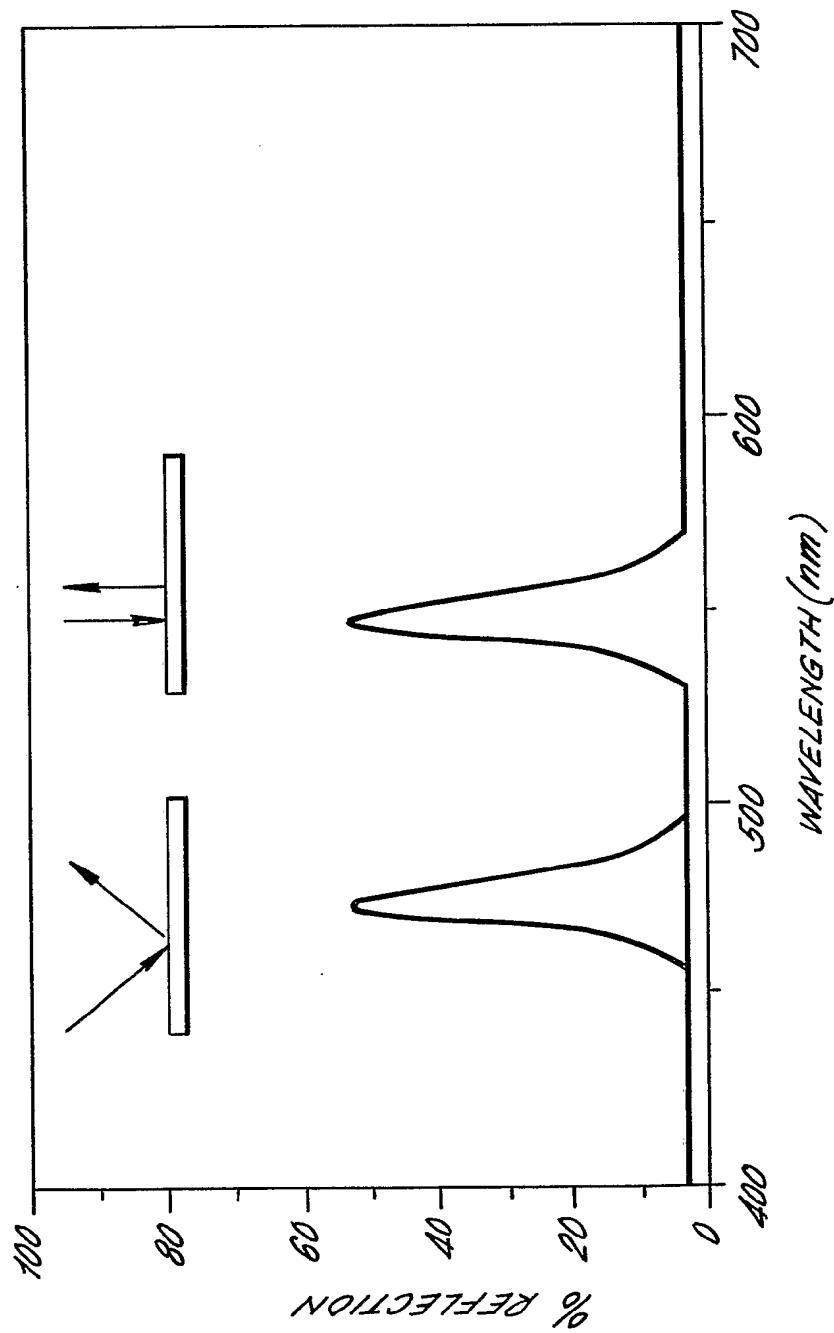
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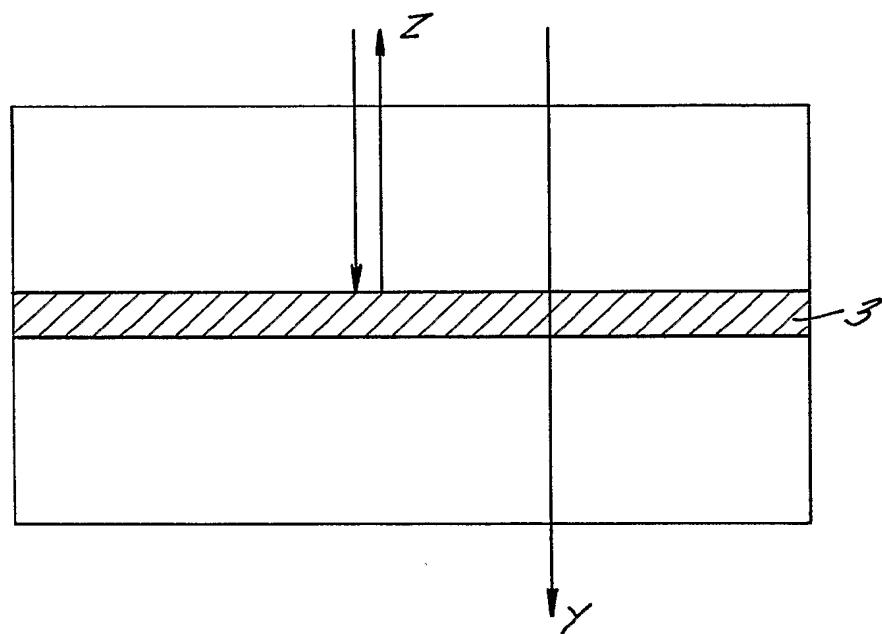
FIG. 1.



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FIG. 2.



*3/5**FIG. 3.*

4/5

FIG. 4.

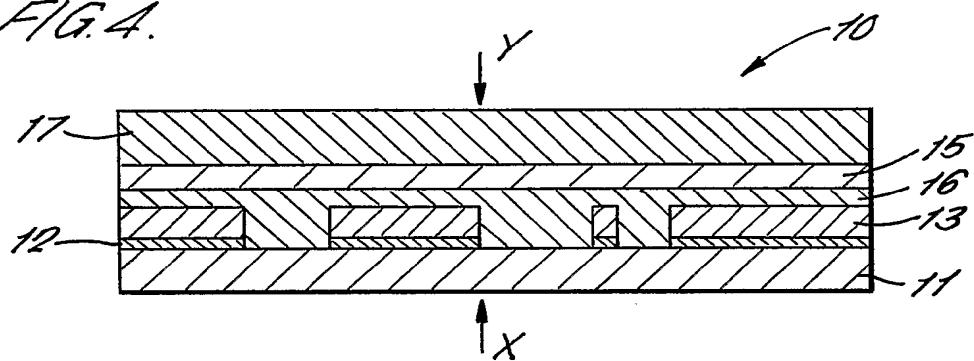


FIG. 5.

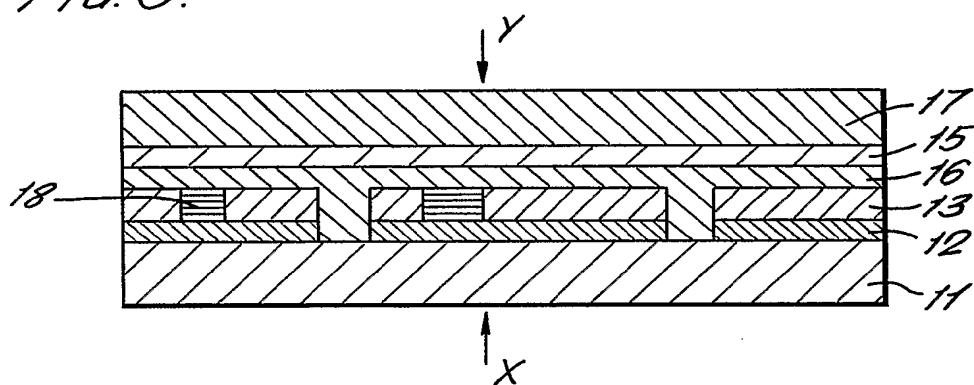
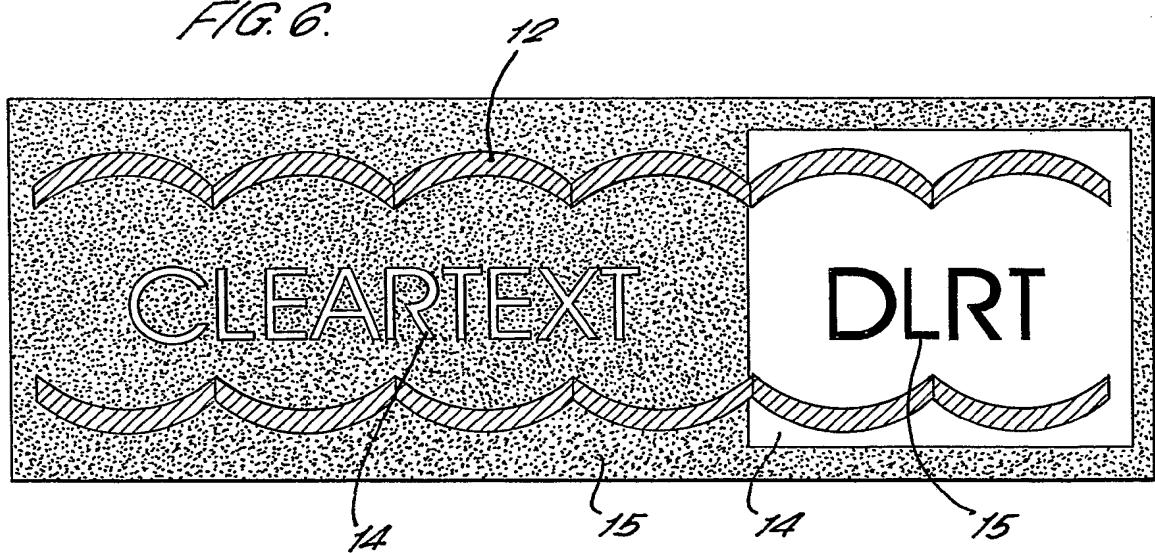


FIG. 6.



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FIG. 7.

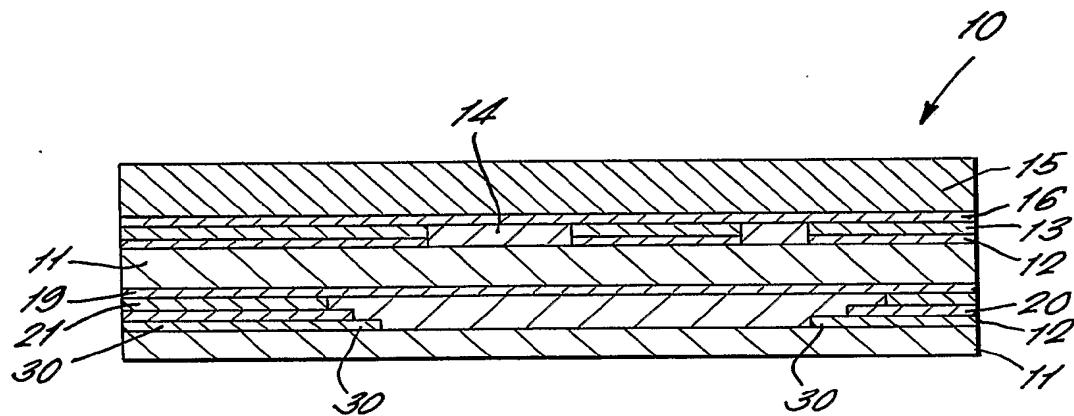
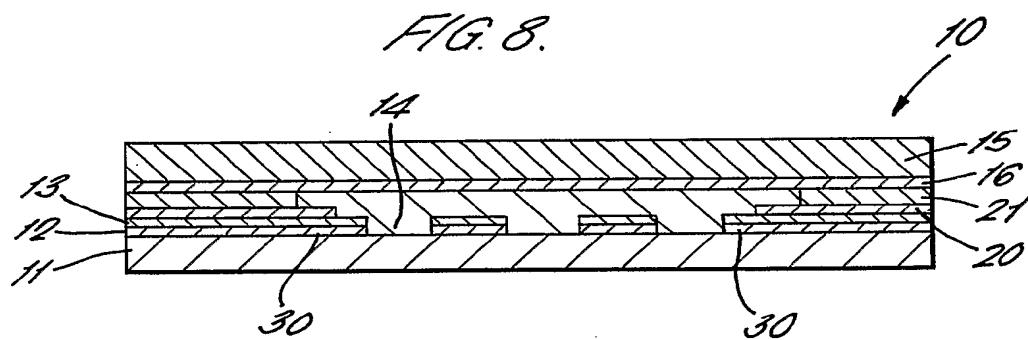


FIG. 8.



## INTERNATIONAL SEARCH REPORT

International Application No  
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A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 B41M3/14 B42D15/00 D21H21/42 D21H21/48

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 318 758 B1 (KAULE WITTICH ET AL) 20 November 2001 (2001-11-20) figure 2 column 2, line 33 -column 5, line 30 column 6, line 22 - line 38 figures 6A-6E ---	1-24
Y	WO 00 39391 A (RIDYARD STEPHEN DAVID ;RUE DE INT LTD (GB); ISHERWOOD ROLAND (GB)) 6 July 2000 (2000-07-06) claims 9,14 page 6, line 24 - line 29 page 13, line 9 - line 20 page 14, line 26 -page 15, line 29 ---	1-24 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 03/00218

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 319 157 A (PORTALS LTD) 7 June 1989 (1989-06-07) cited in the application page 2, line 4-17 examples 4,5,12 ---	1-24
A	EP 0 752 323 A (DAINIPPON PRINTING CO LTD) 8 January 1997 (1997-01-08) column 9, line 6 -column 11, line 28 examples -----	1-24

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No	
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